UNCLASSIFIED

AD NUMBER
AD041152

CLASSIFICATION CHANGES	
TO:	unclassified
FROM:	confidential

LIMITATION CHANGES
TO: Approved for public release; distribution is unlimited.
FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; MAY 1954. Other requests shall be referred to Army Armament Research and Development Center, Dover, NJ.

AUTHORITY
ARRADCOM ltr, 19 Nov 1979; ARRADCOM ltr, 19 Nov 1979

THIS PAGE IS UNCLASSIFIED

C L U D E

GENERAL CLASSIFICATION SCHEDULE
IN ACCORDANCE WITH
...ION SECURITY PROGRAM REGULATION

DATED - JULY 1972

DOD 5000.1R & EXECUTIVE ORDER 11652
(EXECUTIVE ORDER 10501 AMENDED)

BY

Defense Documentation Center
Defense Supply Agency
Cameron Station
Alexandria, Virginia 22314

DEC 1972

UNCLASSIFIED

AD ~~41 152~~

UNCLASSIFIED

Armed Services Technical Information Agency

Because of our limited supply, you are requested to return this copy WHEN IT HAS SERVED YOUR PURPOSE so that it may be made available to other requesters. Your cooperation will be appreciated.

AD

411152

Initial distribution has been made of this report in accordance with distribution list contained herein. Additional distribution may be made to United States military organizations only and are not to be distributed further by them. Requests for this report by other than military organizations may be forwarded to the Office, Chief of Ordnance, Department of the Army, Washington 25, D. C., ATTN: ORDTX-AR, for approval of release. Each request will contain a firm justification based on necessity.

COPY NUMBER **00051**

54AA   61317

REPORT R-1206

A DETERMINATION OF THE PRODUCT RESIDUES AND MAXIMUM
FLAME TEMPERATURES OF SEVERAL PRIMER MIXTURES

Project TSI-11

Prepared by

M. E. LEVY
Chemist

Reviewed by

C. W. DITTRICH
Chief
Propellent Branch

J. W. MITCHELL
Chief
Physical Division

Approved by

E. R. RECHEL
Director
Chemistry Research
Laboratory

C. C. FAWCETT
Director
Pitman-Dunn Laboratories

For

THOMAS J. KANE
Colonel, Ord Corps
Commanding

TABLE OF CONTENTS

ACKNOWLEDGEMENT

OBJECT

To determine the nature of the product residues of the P4, chlorate, styphnate, and zirconium type primer mixture.

To calculate the adiabatic flame temperature of each of these mixtures.

SUMMARY

The product residues remaining in the cup after firing of the P4, chlorate, styphnate, and zirconium type primer mixtures in an open system were determined by X-ray diffraction techniques. The results are presented in the following table, together with comments regarding unaccounted for lines found in the experimental pattern.

Primer Mixture	Type	Components of Residue		
		Definitely Present	Probably Present	Unaccounted for Lines
FA716	P4	$Ba_3(PO_4)_2$ $Ba(NO_3)_2$		Very few
FA90	Chlorate	KCl PbS	Sb_2O_3	Very few
FA875	Styphnate	Pb	β-CaSiO$_3$	Several, indicating additional component, undoubtedly a barium compound
FA878	Zirconium	$BaZrO_3$ ZrO_2	$PbZrO_3$	Considerable number, indicating additional components, probably mixed oxides

The existence of metallic lead in the product residue of the styphnate mixture indicates the oxygen of the air does not enter into this reaction to any significant extent. Due to the great rapidity of this explosive reaction, there is not sufficient time for atmospheric oxygen to diffuse into the reaction zone.

The calculated adiabatic flame temperatures of several primer mixtures are presented in the following table.

Primer Mixture	Type	Condition	Adiabatic Flame Temperature (°K)
FA878	Zirconium	Incomplete oxidation	4080
		Complete oxidation	3940
FA875	Styphnate	Incomplete oxidation	2500
		Complete oxidation	2600
FA70	Chlorate	Incomplete oxidation	2520
		Complete oxidation	2600
FA90	Chlorate	Complete oxidation	2660

Of the three types studied, the zirconium type mixture was found to exhibit the highest calculated adiabatic flame temperature, the highest calculated heat of reaction, and to have the highest proportion of primer products in the molten state at the calculated flame temperature.

AUTHORIZATION

1st Ind, CO 471.83/221, ORDTS, FA 471.836/1561-1, 6 Feb 47

INTRODUCTION

The ability of a primer to ignite a propellant is dependent upon many factors, among them being the mechanism and exothermic character of the explosive reaction.

Rechel,[1]* in a study of primer mixtures, noted that while the primary explosive reaction of a mixture of potassium chlorate and antimony sulfide is assumed to result in the formation of potassium chloride and antimony trioxide, a secondary reaction occurred between potassium chloride and unreacted antimony sulfide forming potassium polysulfide and antimony chloride. The latter then hydrolyzed in water to yield hydrochloric acid, a factor of significance in corrosion of rifle barrels. A similar type of secondary reaction took place when mixtures of lead thiocyanate and potassium chlorate mixtures were caused to react. The residue, consisting of lead sulfide and potassium chloride, underwent secondary reaction to yield potassium sulfide and lead chloride. Basic primer investigations have been conducted by the Franklin Institute[2] under the supervision of the Pitman-Dunn Laboratories of Frankford Arsenal. By means of emission spectra recorded on spectrographic plates, some of the chemical elements, compounds, and radicals formed during the explosion of the FA90, P4, and styphnate type primer mixtures were identified. Wilkinson[3] investigated the thermochemistry of the FA70 and P4 priming mixtures by hot wire ignition in a standard bomb calorimeter and, from the results obtained, postulated the probable products of explosion of these mixtures. Subsequently, portions of the final combustion products of various P4 priming mixtures, ignited by both impact and hot wire, were identified by Kirshner.[4]

While the adiabatic flame temperatures of propellants may be accurately calculated by the use of the method devised by Hirschfelder and his associates,[5] similar calculations for inorganic explosives or incendiaries yield results that can, at best, be accepted as approximations of the true value. This is due to the fact that basic data, such as heat capacities at high temperatures, heats of phase transitions, temperatures at which phase changes occur, and the nature of the reaction mechanism have not been determined to date. The University of Denver[6] has calculated adiabatic reaction temperatures of various incendiary mixtures containing purely inorganic substances. Their results indicated temperatures much higher than would normally be expected. Wilkinson[7] pointed out that these apparently high temperatures were, at least, partly due to the fact that the authors did not consider the heats of fusion and vaporization of the products in calculating the enthalpy of the reaction, nor did they account for the fact that many molecular species undergo dissociation above 3000° K. Theoretical calculations of the performance properties of lithium and boron compounds, acting as rocket fuels in combination with stoichiometric amounts of ammonium perchlorate oxidizer, were carried out by Singley and Fohrell.[8] Arthur D. Little, Inc.[9] has calculated the flame temperature of various explosive mixtures, some of which contained

---

*See attached Bibliography.

inorganic substances, such as aluminum, boron, and magnesium. Fisher and Snay[10] have calculated high temperature heat capacity data for the ideal state for various gaseous and solid compounds and elements. The data, adapted to the temperature range of explosions by extrapolating spectroscopic data, are suitable for thermochemical calculations of explosive reactions. Using the sodium line reversal technique, the Franklin Institute[2] has experimentally determined the maximum temperatures attained when FA90, P4, and styphnate type primer mixtures were fired under unconfined conditions. Confinement of the primer explosion, which more closely approximates actual gun conditions, undoubtedly would yield higher temperatures. However, line reversal techniques are not applicable to the conditions existing in an actual gun, as the presence of propellant in the cartridge case precludes an optical path which is necessary for the line reversal method.[11]

This report concerns the identification of the solid residues of various priming mixtures fired in an open system. Identification was accomplished by the application of X-ray diffraction, a method which permits the determination of the state of chemical combination of the elements present. A knowledge of the nature of the residue may aid in the understanding of the manner in which the primer undergoes explosive reaction. In addition, adiabatic flame temperatures of these primer mixtures were calculated in an effort to determine whether there were substantial differences in the maximum temperatures attained by different primers. To present the results in logical fashion, this report will be divided into two parts:

I.   X-ray diffraction studies;

II. Maximum flame temperature calculations.

2

Part I. Identification of Primer Product Residues by X-Ray Diffraction Techniques

METHODS

X-ray diffraction patterns of the residues remaining in the cups after firing of the FA716, FA90, FA878, and FA875 primer mixtures were taken. The patterns were then interpreted and the components of the residues identified.

To permit easy and rapid insertion of unfired primer cups and removal of the fired primers, the primer cavities of the cartridge cases used in this study were slightly enlarged The FA716 and FA90 primers were initiated by impact, while the FA878 and FA875 were electrically initiated. A sufficient number of primers of each type were fired in this open system to accumulate enough residue for analysis. The samples were loaded, in powder form, into glass capillary tubes and exposed for approximately 12 hours in either a General Electric or North American-Philips X-ray diffraction unit. After the films were developed, the patterns and intensities were recorded, and the "d" values determined. The components of the residue were ascertained by comparing the experimentally obtained patterns with those listed in the standard reference source.[12]

Following are the compositions of the various primer mixtures studied in this report:

Table I. Nominal Composition of Primer Mixtures

FA716 (P4 type)

77 per cent barium nitrate, $Ba(NO_3)_2$

18 per cent stabilized red phosphorus, P

5 per cent trinitrotoluene, $C_6H_2CH_3(NO_2)_3$

FA90 (chlorate type)

53 per cent potassium chlorate, $KClO_3$

12 per cent antimony sulfide, Sb_2S_3

25 per cent lead thiocyanate, $Pb(SCN)_2$

10 per cent pentaerythritol tetranitrate, $C(CH_2ONO_2)_4$

FA70 (chlorate type)

53 per cent potassium chlorate, $KClO_3$

17 per cent antimony sulfide, Sb_2S_3

25 per cent lead thiocyanate, $Pb(SCN)_2$

5 per cent trinitrotoluene, $C_6H_2(NO_2)_3CH_3$

3

Table I. Nominal Composition of Primer Mixtures (Cont'd)

FA875 (styphnate type)

40 per cent lead styphnate, $C_6H_4O_2Pb(NO_2)_3$

14 per cent calcium silicide, $CaSi_2$

44 per cent barium nitrate, $Ba(NO_3)_2$

 1 per cent acetylene black, C

FA878 (zirconium type)

32.5 per cent zirconium, 100 - 325 mesh, Zr

 7.5 per cent zirconium, 120 grade, Zr

20 per cent lead dioxide, PbO_2

20 per cent barium nitrate, $Ba(NO_3)_2$

20 per cent pentaerythritol tetranitrate, $C(CH_2ONO_2)_4$

The FA716 mixture was of the type used in a caliber .30 round, the FA90 was used in conjunction with a caliber .50 round, while the FA878 and FA875 mixtures were designed for use in caliber .60 and 20 mm rounds.

RESULTS

P4 Type Primer Mixture

The X-ray diffraction pattern of the solid residue of the FA716 primer mixture is presented in Figure 1.

Neg. #25008-1
R-1206

Figure 1. FA716 product residue, iron target

Listed below, in Table II, are the interplanar spacings ("d" values) and estimated line intensities (as determined by visual inspection) of this powder pattern, together with the patterns of those substances which account for the experimentally determined values.[12]

4

Table II.   X-Ray Diffraction Pattern of FA716 Residue and of Those
Substances Accounting for Pattern

FA716 Residue		$Ba(NO_3)_2$		$Ba_3(PO_4)_2$	
d Å	Intensity**	d Å	Intensity	d Å	Intensity
4.89	W*				
4.62	S	4.69	75	4.44	9
4.12	S	4.06	30	4.28	12
3.89	W			3.81	7
3.71	W	3.62	15		
3.52	W			3.50	9
3.35	W (β of 3.07)	3.31	10	3.38	17
3.07	VVS			3.08	100
2.96	W			2.97	33
2.85	W	2.87	40		
2.70	W (β of 2.44)				
2.57	W (β of 2.34)				
2.44	VS	2.44	100	2.47	4
2.34	S	2.34	50	2.34	4
2.28	VW			2.28	7
				2.21	3
2.13	E			2.13	23
2.08	W			2.07	11
2.03	W	2.02	20	2.03	17
				1.97	13
1.92	W			1.92	17

*Lines not accounted for by suggested nature of residue.

**The symbols used to denote intensities are as follows:
  VVS - very, very strong; VS - very strong; S - strong;
  MS - medium strong; M - medium; MW - medium weak;
  W - weak; VW - very weak; VVW - very, very weak.

5

Table II. X-Ray Diffraction Pattern of FA716 Residue and of Those
Substances Accounting for Pattern (Cont'd)

FA716 Residue		$Ba(NO_3)_2$		$Ba_3(PO_4)_2$	
$d\ \mathring{A}$	Intensity**	$d\ \mathring{A}$	Intensity	$d\ \mathring{A}$	Intensity
1.86	W	1.86	40		
1.81	W	1.81	30		
1.73	W			1.73	3
1.66	W	1.65	30	1.67	7
1.62	VW*				
1.59	VW			1.60	17
1.56	M	1.56	30	1.56	12
1.48	VVW				
1.45	VVW	1.43	15	1.43	1
1.40	VVW			1.39	7
1.37	MW	1.37	40	1.36	9
1.35	W	1.35	10	1.34	7
		1.32	1		
1.28	VVW	1.28	8	1.28	3
				1.26	3
1.24	VVW	1.24	13		
1.23	VVW	1.22	13	1.23	3
		1.17	4		
1.14	VVW	1.14	10		
1.13	W	1.13	6		
1.09	W	1.09	13		
1.05	W	1.06	20		

*Lines not accounted for by suggested nature of residue.
**The symbols used to denote intensities are as follows:
  VVS - very, very strong; VS - very strong; S - strong;
  MS - medium strong; M - medium; MW - medium weak;
  W - weak; VW - very weak; VVW - very, very weak.

It is seen that the reflections of barium nitrate, $Ba(NO_3)_2$, and barium ortho-phosphate, $Ba_3(PO_4)_2$, account for practically all the lines in the pattern of the residue. There remain but a few weak lines which are not accounted for by either of the above compounds. The weakness of these lines shows they are due to some substance or substances not present in substantial amounts. The presence of barium nitrate in the cup after firing indicates the primer explosion is characterized by incomplete combustion. The strong intensity of the barium nitrate lines also indicates a substantial amount of the reactant did not enter into the reaction, possibly due to an excess of barium nitrate in the mixture. Wilkinson[2] had postulated this incomplete reaction to be characteristic of mixtures containing more than 80 per cent barium nitrate (considering merely the barium nitrate-phosphorus binary mixture). Kirshner[4] found small amounts of barium nitrate in the residue of binary mixtures containing as little as 75 per cent barium nitrate. While the results of Wilkinson and Kirshner pertain to firings conducted in essentially closed systems, those discussed in this report were carried out in an open system. The presence of the salt, barium orthophosphate, is undoubtedly due to a reaction between basic barium oxide and acidic phosphorus oxide, two intermediate products.

Chlorate Type Primer Mixture

The diffraction pattern of the residue remaining in the cup after firing the FA90 primer mixture is shown in Figure 2, while the "d" values and estimated line intensities of this pattern, together with those of substances accounting for the experimental values are listed in Table III.

Neg. #25008-2
R-1206
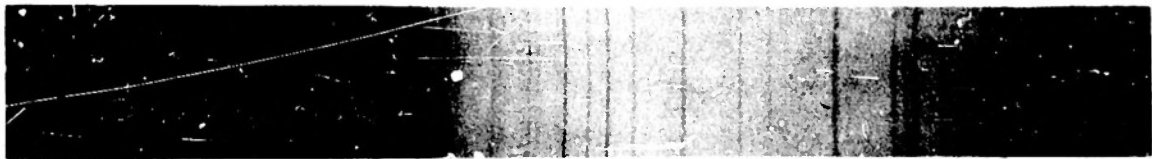
Figure 2. FA90 product residue, nickel target

7

Table III. X-Ray Diffraction Pattern of FA90 Residue and of Those
Substances Accounting for Pattern

| FA90 Residue | | KCl | | Sb_4O_6 | | Sb_6O_{10} | | PbS | |
d Å	Intensity**	d Å	Intensity	d Å	Intensity	d Å	Intensity	d Å	Intensity
3.72	W (β of 3.37)					6.0	100		
3.64	W (β of 3.30)								
3.42	W (β of 3.10)							3.43	80
3.37	MS								
3.30	MS			3.22	100				
3.24	W (β of 2.93)								
3.16	W*								
3.10	S	3.12	100			3.10	80		
2.99	W*								
2.93	MS					2.97	80	2.97	100
2.82	VW*								
2.76	VW			2.78	30				
2.54	VW			2.56	8	2.58	16		
2.43	MS (β of 2.20)					2.36	4		
2.29	W (β of 2.08)								
2.20	VS	2.21	67						

*Lines not accounted for by suggested nature of residue.
**The symbols used to denote intensities are as follows:
VVS - very, very strong; VS - very strong; S - strong; MS - medium strong;
M - medium; MW - medium weak; W - weak; VW - very weak; VVW - very, very weak.

8

Table III. X-Ray Diffraction Pattern of FA90 Residue and of Those
Substances Accounting for Pattern (Cont'd)

| FA90 Residue | | KCl | | Sb₄O₆ | | Sb₄O₁₀ | | PbS | |
d Å	Intensity**	d Å	Intensity	d Å	Intensity	d Å	Intensity	d Å	Intensity
2.14	VW*								
2.11	VW*								
2.08	S							2.09	60
2.05	W*								
2.03	W*								
1.96	W			1.96	50	1.98	16		
1.91	VW*								
1.88	VW*								
1.80	MS	1.81	20			1.82	50		
1.78	S							1.79	32
1.70	VS					1.73	16	1.71	16
1.68	W			1.68	50				
1.66	W*								
1.56	MS	1.57	6	1.56	10	1.55	36		
1.55	W								
1.48	W					1.48	8	1.48	8
1.46	W			1.45	2	1.44	8		

*Lines not accounted for by suggested nature of residue.
**The symbols used to denote intensities are as follows:
VVS - very, very strong; VS - very strong; S - strong; MS - medium strong;
M - medium; MW - medium weak; W - weak; VW - very weak; VVW - very, very weak.

9

Table III. X-Ray Diffraction Pattern of FA90 Residue and of Those Substances Accounting for Pattern (Cont'd)

FA90 Residue		KCl		Sb₄O₆		Sb₄O₁₀		PbS	
d Å	Intensity**	d Å	Intensity	d Å	Intensity	d Å	Intensity	d Å	Intensity
1.41	VW*								
1.40	MS	1.40	12	1.39	6				
1.35	M			1.36	4			1.36	8
1.33	VW					1.34	12	1.33	16
1.32	MS								
1.28	MS	1.28	6	1.28	15				
1.26	W			1.25	10				
1.24	W*								
1.22	W			1.22	1			1.21	8
1.20	MS					1.18	8		
1.14	MS			1.14	7	1.15	4	1.14	8
1.11	W	1.11	2						
1.09	W			1.07	8	1.08	4		
1.04	S	1.05	2	1.05	70	1.05	4	1.05	4

*Lines not accounted for by suggested nature of residue.
**The symbols used to denote intensities are as follows:
VVS - very, very strong; VS - very strong; S - strong; MS - medium strong;
M - medium; MW - medium weak; W - weak; VW - very weak; VVW - very, very weak.

10

Although a considerable number of lines remain unaccounted for, it should be noted that they are all either weak or very weak, indicating the substance or substances causing them are not present in substantial amounts. As none of the reactants were found in the residue, it is seen that the FA90 primer undergoes complete combustion. Potassium chloride and lead sulfide are definitely present, while the presence of antimony trioxide is indicated. At best, there may be a small amount of antimony pentoxide, but its presence is open to question. The existence of potassium chloride is undoubtedly due to the dissociation of potassium chlorate, thus liberating large amounts of oxygen which enter into the explosive reaction. It should be noted that the minimum concentration of material in a mixture which can be detected by the use of X-ray diffraction methods is usually about five to ten per cent. Therefore, the results obtained in this investigation do not preclude the existence of small amounts of secondary reaction products as determined by Rechel.[1]

Styphnate Type Primer Mixture

Figure 3 illustrates the diffraction pattern of the residue of the FA875 primer mixture remaining in the cup after firing.

Neg. #25008-3
R-1206

Figure 3. FA875 product residue, copper target

The experimental "d" values and line intensities are shown in Table IV along with those of the substances accounting for most of the experimental pattern.

11

Table IV. X-Ray Diffraction Pattern of FA875 Residue and of Those
Substances Accounting for Pattern

FA875 Residue		Pb		β-CaSiO$_3$	
d Å	Intensity**	d Å	Intensity	d Å	Intensity
4.57	W*				
3.98	W*				
				3.83	20
3.60	W*				
				3.51	40
3.26	W*				
				3.20	10
3.11	W (β of 2.82)			3.10	40
2.97	W			2.98	100
2.82	VS	2.82	100		
2.45	S	2.44	80	2.46	20
2.41	S*				
				2.34	10
2.31	M			2.30	10
				2.18	20
2.11	W*				
2.03	VW*				
2.00	W			2.01	10
				1.98	10
1.91	W (β of 1.73)				
1.84	W			1.83	60
1.79	W			1.79	10
1.73	S	1.74	80	1.75	20
				1.71	20
1.64	W*				
				1.60	20

*Lines not accounted for by suggested nature of residue.
**The symbols used to denote intensities are as follows:
  VVS - very, very strong; VS - very strong; S - strong; MS - medium strong;
  M - medium; MW - medium weak; W - weak; VW - very weak; VVW - very, very weak.

Table IV. X-Ray Diffraction Pattern of FA875 Residue and of Those
Substances Accounting for Pattern (Cont'd)

FA875 Residue		Pb		β-CaSiO₃	
d Å	Intensity**	d Å	Intensity	d Å	Intensity
1.55	W			1.53	10
1.50	W*				
1.48	S	1.48	100	1.47	10
				1.45	10
1.42	W	1.42	30		
1.36	W			1.36	10
1.34	W			1.34	10
				1.26	10
1.23	VW	1.23	70		
1.13	VW	1.13	70		
1.10	VW	1.10	50		
1.05	VW*				
1.00	VW	1.01	50		
0.98	VW*				
0.95	VW	0.948	30		

*Lines not accounted for by suggested nature of residue.
**The symbols used to denote intensities are as follows:
VVS - very, very strong; VS - very strong; S - strong; MS - medium strong;
M - medium; MW - medium weak; W - weak; VW - very weak; VVW - very, very weak.

It is seen from Table IV that only lead may be conclusively shown to be present, while
a small amount of beta-calcium silicate may be present. A line of strong intensity
and quite a few weak lines remain unaccounted for by lead and beta-calcium silicate,
indicating the presence of a significant amount of an unidentified component(s) of the
residue, which is undoubtedly a barium containing compound. Examination of the refer-
ence literature[12] revealed no possible substance which would account for these lines.
The existence of metallic lead rather than lead of a higher oxidation state in the
product residue of this primer, indicates the presence of a reducing atmosphere in the
reaction zone. This could only occur if the atmospheric oxygen does not enter into the
explosive reaction to any appreciable extent. It therefore follows that, basically,
the only oxygen involved in the reaction is that initially present in the primer mix-
ture. The rapidity with which the reaction occurs (due to the rapid decomposition of
lead styphnate) probably does not permit sufficient time for atmospheric oxygen to

13

diffuse into the reaction zone. Comparable results were obtained by the University of Denver[6] in their study of incendiary mixtures in which they concluded that the surrounding atmosphere did not enter appreciably into the explosion of certain incendiary mixtures, such as the IM-11, which has the composition 50 per cent magnesium-aluminum alloy and 50 per cent barium nitrate.

Zirconium Type Primer Mixture

The X-ray diffraction pattern of the residue remaining in the cup after firing of the FA878 primer mixture is illustrated in Figure 4.

Neg. #25008-4
R-1206

Figure 4. FA878 product residue, copper target

Table V lists the "d" values and line intensities of the above pattern together with those of the compounds accounting for the pattern.

Table V. X-Ray Diffraction Pattern of FA878 Residue and of
Those Substances Accounting for Pattern

FA878 Residue		BaZrO$_3$		PbZrO$_3$		ZrO$_2$	
d Å	Intensity**	d Å	Intensity	d Å	Intensity	d Å	Intensity
2.90	S	2.97	100	2.93	100	2.96	100
2.79	W*						
2.71	W (β of 2.44)						
2.63	W*						
2.56	W						2.56	24

*Lines not accounted for by suggested nature of residue.
**The symbols used to denote intensities are as follows:
  VVS - very, very strong; VS - very strong; S - strong; MS - medium strong;
  M - medium; MW - medium weak; W - weak; VW - very weak; VVW - very, very weak.

14

Table V.   X-Ray Diffraction Pattern of FA878 Residue and of
Those Substances Accounting for Pattern (Cont'd)

FA878 Residue		BaZrO$_3$		PbZrO$_3$		ZrO$_2$	
d Å	Intensity**	d Å	Intensity	d Å	Intensity	d Å	Intensity
2.44	VVS*						
2.40	W	2.42	40	2.39	40		
2.27	M (β of 2.07)						
2.10	W	2.09	70	2.09	70		
2.07	S			2.06	60		
1.98	W (β of 1.79)						
1.89	S*						
1.86	W			1.85	10		
1.79	VS					1.81	80
				1.76	20		
1.73	W*						
1.69	VS	1.71	80	1.69	100		
1.61	VS*			1.61	10		
1.55	VW*						
1.53	W					1.54	60
1.49	W			1.50	10	1.48	10
1.46	VS	1.48	70	1.46	90		
				1.41	10		
1.37	S			1.38	20		
1.35	S	1.33	70				
1.31	S			1.32	60		
1.29	VW					1.28	12
		1.26	20				
1.23	M*						
1.20	M	1.21	60	1.19	60		
1.17	W					1.17	20
1.15	W					1.14	12

*Lines not accounted for by suggested nature of residue.
**The symbols used to denote intensities are as follows:
  VVS - very, very strong; VS - very strong; S - strong; MS - medium strong;
  M - medium; MW - medium weak; W - weak; VW - very weak; VVW - very, very weak.

Table V.   X-Ray Diffraction Pattern of FA878 Residue and of
Those Substances Accounting for Pattern (Cont'd)

FA878 Residue		BaZrO₃		PbZrO₃		ZrO₂	
d Å	Intensity**	d Å	Intensity	d Å	Intensity	d Å	Intensity
1.13	W			1.12	20		
1.11	S	1.12	80	1.11	100		
1.09	M			1.09	10		
				1.07	10		
1.05	W	1.05	50	1.05	10		
1.04	MS			1.04	10	1.04	16
1.02	M*						
1.01	M*						
0.98	M	0.990	70			0.984	14
0.97	W*						
0.93	M	0.938	70				
0.90	M	0.894	70			0.904	5

*Lines not accounted for by suggested nature of residue.
**The symbols used to denote intensities are as follows:
  VVS - very, very strong; VS - very strong; S - strong; MS - medium strong;
  M - medium; MW - medium weak; W - weak; VW - very weak; VVW - very, very weak.

None of the patterns of the reactants fit that of the residue, therefore it is
seen that the FA878 primer mixture exhibits complete combustion. Examination of the
above table definitely indicates the presence of the mixed oxide, barium zirconate
and, in all probability, lead zirconate. Zirconium dioxide is also seen to be present.
There are, however, many lines which are not accounted for by the above products.
These are probably due to other mixed oxides whose patterns are not listed in the
reference source of X-ray diffraction patterns.[12]

DISCUSSION OF X-RAY DIFFRACTION
IN CHEMICAL ANALYSIS

The use of X-ray diffraction in chemical analysis offers the important advantage
of permitting the determination of the presence of compounds and elements. In addition,
the method of analysis is nondestructive and requires but very small amounts of ma-
terial. On the other hand, there are definite limitations. The method is only appli-
cable to crystalline solid materials whose powder patterns are known. It is important

16

that the pattern produced by a substance be fairly strong, or else it might go un-
noticed in the analysis of a mixture of unknowns. The sensitivity of analysis by X-ray
diffraction is not great, a concentration of five to ten per cent being the minimum
amount detectable for most substances. In addition, elements may be present in solid
solutions to a large extent and still not alter the pattern of the matrix material
sufficiently to permit detection of the element. In other words, while the presence
of a material may be confirmed. it is not possible to conclusively show the absence of
a substance. Finally, the more the components in the unknown, the more difficult is
the interpretation of the experimental pattern. At most, the sample should consist of
but four major components.

CONCLUSIONS

1. The nature of the various residues remaining in the cup after firing of the
primer mixtures in an open system are presented in the following table, along with
comments regarding lines in the experimental patterns not accounted for by the identi-
fied components.

| | | Components of Residue | | |
Primer Mixture	Type	Definitely Present	Probably Present	Unaccounted for Lines
FA716	P4	$Ba_3(PO_4)_2$ $Ba(NO_3)_2$		Very few and of weak intensity, indicating them to be due to substance or sub- stances not present in substantial amounts
FA90	Chlorate	KCl PbS	Sb_2O_3	Weak intensity, in- dicating them to be due to substance or substances not present in substantial amounts
FA875	Styphnate	Pb	β-$CaSiO_3$	One strong line and several weak lines in- dicating presence of significant amount of another component, un- doubtedly a barium con- taining compound
FA878	Zirconium	$BaZrO_3$ ZrO_2	$PbZrO_3$	Several strong and medium intensity lines indicating presence of at least one unidentified component, probably a mixed oxide

17

   2.   The existence of metallic lead in the product residue of the FA875 (styphnate) primer mixture indicates atmospheric oxygen does not enter into the reaction to any appreciable extent and that, basically, the only oxygen involved in the explosive reaction of the styphnate primer mixture is that initially present in the mixture.

   3.   The FA716 primer mixture exhibited incomplete combustion when fired in an open system.

18

PART II. ADIABATIC FLAME TEMPERATURE CALCULATIONS OF
SEVERAL PRIMER MIXTURES

METHODS AND PROCEDURES

The maximum flame temperature of a pr   xplosive reaction serves to partly in-
dicate the rate of heat transfer from the ʖ   .er to the propellant, a factor of impor-
tance in determining propellent ignition properties of various primers. As discussed
in the introduction, factors such as the heat of reaction of the primer explosion, the
mechanism and extent of reaction, the heat capacities at high temperatures of the prod-
ucts, the nature and energies involved in the phase transitions of the various products,
and the stability of the products must be known before any accurate calculations of
maximum flame temperatures can be carried out. In view of the lack of information re-
garding much of the above basic data, adiabatic flame temperature calculation for in-
organic primer mixtures can, at best, be regarded as good approximations of the true
value. To carry out the calculations described in this report, it was necessary to
extrapolate the available specific heat data to very high temperatures, and through one
or two phase changes (since very little heat capacity data are available regarding
molten or vaporized inorganic compounds) and in one case, to make a logical estimate
as to the heat of phase transition. The heat capacities of practically all solids and
liquids are reported in the literature as heat capacity at constant pressure, C_p. How-
ever, for solids and liquids, there is very little difference between the above value
and the heat capacity at constant volume, C_v. As a result, no significant error is in-
troduced by equating C_p and C_v for solids and liquids.

It is assumed that the reaction occurs instantaneously under constant volume con-
ditions, goes to completion, and takes place so rapidly that no heat is lost to the
surroundings during the reaction. Consequently, the calculated temperatures should be
regarded as the *maximum* flame temperatures. In regard to the nature of the products,
the metallic constituents of the primer are assumed to exist in the form of their oxides
at the explosion temperatures, while nitrogen exists as nitrogen gas. It is known that
metallic oxides are more stable at high temperatures than their corresponding nitrides,
carbides, or sulfides, while the nitrogen oxides are less stable at high temperatures
than the metallic oxides.

The phase changes of the products and the corresponding heats of fusion and vapor-
ization were considered, when necessary, in the calculations. The flame temperature
was first calculated assuming no phase changes. If this temperature proved to be higher
than the melting or boiling point of any of the products, the heat required to melt and,
if necessary, to vaporize the given amount of product was deducted from the available
energy, and a more accurate flame temperature was then calculated. The calculations
are based on the primer mixture reacting at room temperature and the resulting products

then being heated to the adiabatic flame temperature. The flame temperature is:

$$T_{flame} = T_{initial} + \frac{Q_v - \Sigma L_p}{\Sigma C_v} \qquad (1)$$

where Q_v represents the heat of reaction at constant volume, ΣL_p denotes the latent heats of fusion (and vaporization, if necessary) of the products, and ΣC_v denotes the heat capacities of the products, i. e., the energy required to raise the products from $T_{initial}$ to T_{flame}. Latent heats at constant volume and constant pressure were assumed equal. This assumption does not significantly affect the results, which are interpreted on a comparative basis.

Calculations were carried out for two extreme conditions. In one case, it was assumed that the oxygen of the air enters into the reaction, causing the products to be formed in their highest oxidation state as dictated by stability. The nitrogen in the reacting volume of air remains unaltered and is merely raised to the adiabatic flame temperature. This condition is defined as "complete oxidation." The other condition, "incomplete oxidation," assumes that only the oxygen initially present in the primer mixture enters into the reaction, and that preferential oxidation occurs in the following order:

(1) Oxidation of a metal to its oxide
(2) Oxidation of carbon to carbon monoxide
(3) Oxidation of hydrogen to water
(4) Oxidation of carbon monoxide to carbon dioxide

The last three stages are in accordance with the Kistiakowsky-Wilson assumptions.[9]

In view of the approximations previously discussed, the refinement of correcting for molecular dissociation of the product gases was not introduced. This would only become significant at temperatures above 3000° K. Introduction of this correction would serve to slightly lower those calculated temperatures in excess of 3000° K.

The thermochemical data used in these calculations, together with their source of reference, are presented in the following tables.

Table VI. Heats of Formation

Material	State	Heat of Formation, $-\Delta H_f^{298}$ (kcal/mole)	Reference
BaO	s	133.4	13
Ba(NO$_3$)$_2$	s	237.05	13
CaO	s	151.9	13
CaSi$_2$	s	224.6	17

20

Table VI.   Heats of Formation (Cont'd)

Material	State	Heat of Formation, $-\Delta H_f^{298}$ (kcal/mole)	Reference
SiO_2	s	202.5	13
PbO	s	52.4	13
PbO_2	s	66.12	13
$Pb(CNS)_2$	s	-27.5	13
$PbC_6H(NO_2)_3O_2$	s	-92.3	16
Sb_2S_3	s	43.5	13
Sb_2O_3	s	168.4	13
Sb_2O_5	s	234.4	13
ZrO_2	s	258.2	13
$KClO_3$	s	93.50	13
KCl	s	104.175	13
$C(CH_2NO_3)_4$	s	123.3	5
CO	g	26.690	5
CO_2	g	94.030	5
H_2O	g	57.502	5
SO_2	g	70.96	5

Table VII.   Thermochemical Constants

Material	Melting Point (°K)	Heat of fusion, (kcal/mole)	Boiling Point (°K)	Heat of Vaporization (kcal/mole)	Reference
PbO	1159	2.8	1745	51	13
BaO	2190	*	2273	90	17, 19
CaO	2873	12	3123	42.57	13, 18
SiO_2	1883	2.31	2503	79	13, 18, 19
ZrO_2	2950	20.8	4573		13, 17
KCl	1045	6.1	1680	38.8	13
Sb_4O_6	928	29.49	1729	17.83	13

*Heat of fusion of BaO assumed equal to that of CaO

21

Table VIII. Heat Capacity Data

Material	State	$C_p = a + b \times 10^{-3}T - c \times 10^5 T^{-2}$			Range ($°K$)	Reference
		a	b	c		
CaO	s	10.00	4.84		273-1173	14
PbO	s	10.33	3.18		273-544	14
BaO	s	10.98	1.42			6
ZrO_2	s	11.62	10.46	1.777	273-1673	15
Sb_2O_3	s	19.1	17.1		273-929	14
SiO_2	s	12.80	4.47		273-1973	14
KCl	s	10.93	3.76		273-1043	14
SO_2	g	7.70	5.30		300-2500	14

Heat capacities of CO, CO_2, H_2, O_2, N_2, and $H_2O(g)$ were determined from the tables in Hirschfelder's report.[5] An average value of $\gamma = 1.25$ was estimated for $SO_2(g)$.[17]

The following example will serve to illustrate the methods employed in these calculations:

Primer mixture: FA878   Condition: incomplete oxidation

Composition:

    40 per cent zirconium, Zr

    20 per cent barium nitrate, $Ba(NO_3)_2$

    20 per cent pentaerythritol tetranitrate, $C(CH_2NO_3)_4$

    20 per cent lead dioxide, PbO_2

Molecular (or atomic) weight:

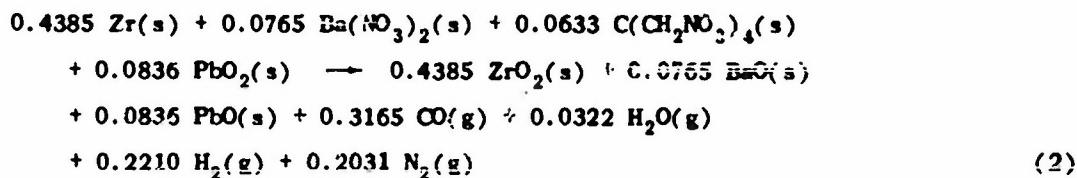|		
Zr	91.22	grams/gram atom
$Ba(NO_3)_2$	261.38	grams/mole
$C(CH_2NO_3)_4$	316.15	"
PbO_2	239.21	"

Moles of each component in 100 grams primer mixture:

    40 grams Zr = 40/91.22 = 0.4385 gram atoms/100 grams

    20 grams $Ba(NO_3)_2$ = 20/261.38 = 0.0765 moles/100 grams

    20 grams $C(CH_2NO_3)_4$ = 20/316.15 = 0.0633 moles/100 grams

    20 grams PbO_2 = 20/239.21 = 0.0836 moles/100 grams

22

Preferential oxidation of the products occurs as follows:

(1) $Zr \longrightarrow ZrO_2$, $Ba \longrightarrow BaO$, and $Pb \longrightarrow PbO$

(2) $C \longrightarrow CO$

(3) $H \longrightarrow H_2O$

(4) $CO \longrightarrow CO_2$

The reaction may therefore be described as:

$$0.4385\ Zr(s) + 0.0765\ Ba(NO_3)_2(s) + 0.0633\ C(CH_2NO_3)_4(s)$$
$$+ 0.0836\ PbO_2(s) \longrightarrow 0.4385\ ZrO_2(s) + 0.0765\ BaO(s)$$
$$+ 0.0836\ PbO(s) + 0.3165\ CO(g) + 0.0322\ H_2O(g)$$
$$+ 0.2210\ H_2(g) + 0.2031\ N_2(g) \tag{2}$$

The heat of reaction of the above, in kilocalories/100 grams is therefore:

$$\Delta H \text{ reaction} = H \text{ products} - H \text{ reactants}$$

$$\Delta H_1 = [\ \overset{ZrO_2}{(0.4385)\ (258.2)} + \overset{BaO}{(0.0765)\ (133.4)} + \overset{PbO}{(0.0836)\ (52.4)}$$
$$+ \overset{CO}{(0.3165)\ (26.690)} + \overset{H_2O}{(0.0322)\ (57.502)}\ ]$$
$$- [\ \overset{Ba(NO_3)_2}{(0.0765)\ (237.06)} + \overset{C(CH_2NO_3)_4}{(0.0633)\ (123.2)}$$
$$+ \overset{PbO_2}{(0.0836)\ (66.12)}\ ] \tag{3}$$

$$\Delta H_1 = [\ 113.22 + 10.21 + 4.38 + 8.45 + 1.85\ ] - [\ 18.14 + 7.80 + 5.53\ ]$$

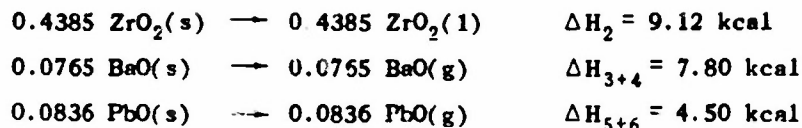$$\Delta H_1 = 106.64 \text{ kcal/100 grams}$$

The reference sources for the above given heats of formation are listed in Table VI. In regard to the product oxides, the following changes of state occur:

$ZrO_2(s) \longrightarrow ZrO_2(1)$ $\Delta H_2 = 20.8$ kcal/mole

$BaO(s) \longrightarrow BaO(1)$ $\Delta H_3 = 12$ kcal/mole*

$BaO(1) \longrightarrow BaO(g)$ $\Delta H_4 = 90.0$ kcal/mole

$PbO(s) \longrightarrow PbO(1)$ $\Delta H_5 = 2.8$ kcal/mole

$PbO(1) \longrightarrow PbO(g)$ $\Delta H_6 = 51$ kcal/mole

---
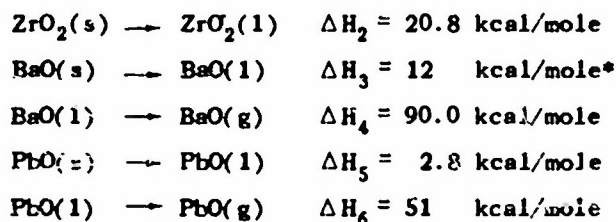
*Latent heat of fusion of BaO assumed to be equal to that of CaO.

23

Therefore

$$0.4385 \ ZrO_2(s) \longrightarrow 0.4385 \ ZrO_2(1) \qquad \Delta H_2 = 9.12 \ \text{kcal}$$

$$0.0765 \ BaO(s) \longrightarrow 0.0765 \ BaO(g) \qquad \Delta H_{3+4} = 7.80 \ \text{kcal}$$

$$0.0836 \ PbO(s) \longrightarrow 0.0836 \ PbO(g) \qquad \Delta H_{5+6} = 4.50 \ \text{kcal}$$

The overall ΔH describing the reaction in which ZrO_2 is liquified, while BaO and PbO are vaporized, is:

$$\Delta H = \Delta H_1 - \Delta H_2 - \Delta H_{3+4} - \Delta H_{5+6} \tag{4}$$
$$= 106.64 - 9.12 - 7.80 - 4.50$$
$$= 85.24 \ \text{kcal}/100 \ \text{grams at the flame temperature.}$$

The energy required to raise the products from $300°$ K to any given temperature, T_2 is:

$$(E_{T_2} - E_{300}) = 0.4385 \left[11.62 \ T + 5.23 \times 10^{-3} T^2 + \frac{1.777 \times 10^5}{T} \right]_{300}^{T_2} \qquad ZrO_2$$

$$+ 0.0765 \left[10.98T + 0.71 \times 10^{-3} \ T^2 \right]_{300}^{T_2} \qquad BaO$$

$$+ 0.0836 \left[10.33T + 1.59 \times 10^{-3} \ T^2 \right]_{300}^{T_2} \qquad PbO$$

$$+ 0.3165 \left[E_{T_2} - E_{300} \ \text{for 1 mole CO} \right] \qquad CO$$

$$+ 0.2031 \left[E_{T_2} - E_{300} \ \text{for 1 mole } N_2 \right] \qquad N_2$$

$$+ 0.0322 \left[E_{T_2} - E_{300} \ \text{for 1 mole } H_2O \right] \qquad H_2O$$

$$+ 0.2210 \left[E_{T_2} - E_{300} \ \text{for 1 mole } H_2 \right] \qquad H_2 \tag{5}$$

A base temperature of $300°$ K, instead of $298°$ K, was used. This simplified the calculations, and introduced no error of significance. The energies required to heat the products to various assumed temperatures, T_2, are shown in the following table.

Table IX. Adiabatic Flame Temperature of FA 878
Primer Mixture (Incomplete Oxidation)

Assumed Temperature, T_2 (°K)	Energy Required to Heat Products to T_2, (kcal/100 grams)	Heat of Reaction Calculated at T_2 (kcal/100 grams)	Adiabatic Flame Temperature, (°K)
3500	67.54	85.24	> 3500
4300	92.91	85.24	< 4300
4100	86.27	85.24	< 4100

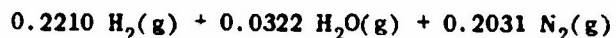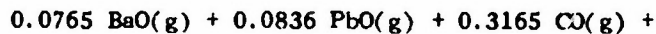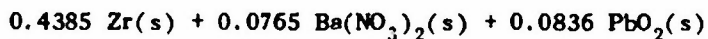Graphically interpolating, it is found that the calculated adiabatic flame temperature is 4080° K.

The above described calculations were carried out for the FA70, FA90, FA875, and FA878 primer mixtures.

The reaction of the FA716 (P4 type) primer mixture probably results in the formation of barium metaphosphate at the explosion temperature.[3] In view of the fact that no heat capacity data are available for this compound, it was not possible to carry out similar calculations for this primer mixture.

RESULTS

The reactions describing the explosive combustion of 100 grams of each of the various primer mixtures are presented below. It is assumed that the reaction goes to completion under constant volume conditions. The states of the products are determined by the flame temperatures.
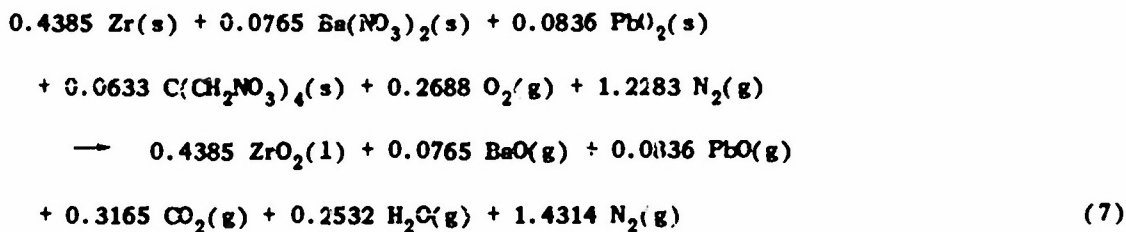
FA878 (Zirconium type)   —   Incomplete oxidation

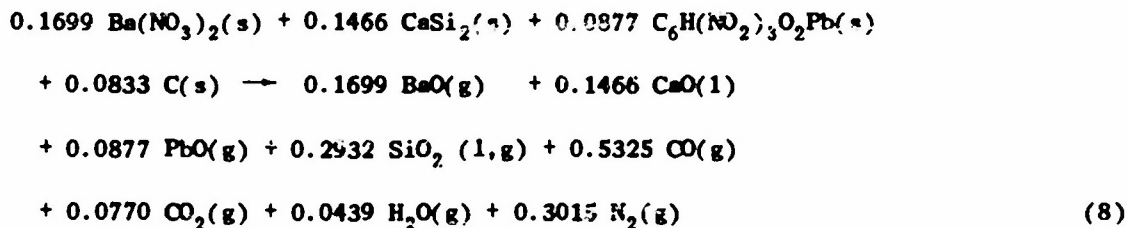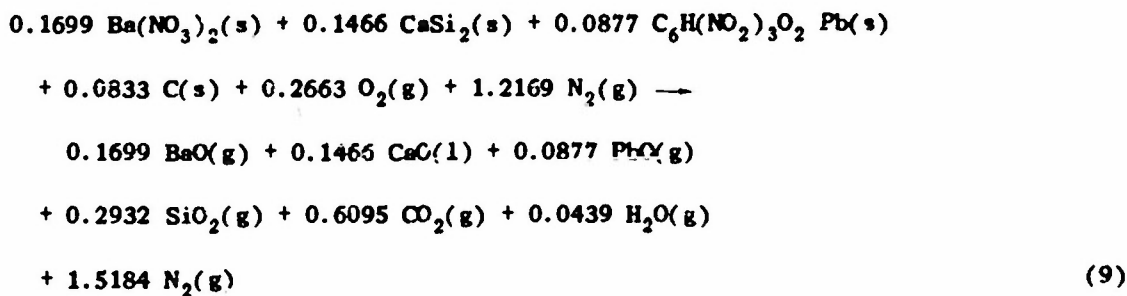$0.4385 \ Zr(s) + 0.0765 \ Ba(NO_3)_2(s) + 0.0836 \ PbO_2(s)$

$+ 0.0633 \ C(CH_2NO_3)_4(s) \longrightarrow 0.4385 \ ZrO_2(1) +$

$0.0765 \ BaO(g) + 0.0836 \ PbO(g) + 0.3165 \ CO(g) +$

$0.2210 \ H_2(g) + 0.0322 \ H_2O(g) + 0.2031 \ N_2(g)$ (6)

25

FA878 (Zirconium type) — Complete Oxidation

$$0.4385 \ Zr(s) + 0.0765 \ Ba(NO_3)_2(s) + 0.0836 \ PbO_2(s)$$

$$+ 0.0633 \ C(CH_2NO_3)_4(s) + 0.2688 \ O_2(g) + 1.2283 \ N_2(g)$$

$$\longrightarrow \ 0.4385 \ ZrO_2(l) + 0.0765 \ BaO(g) + 0.0836 \ PbO(g)$$

$$+ 0.3165 \ CO_2(g) + 0.2532 \ H_2O(g) + 1.4314 \ N_2(g) \tag{7}$$

FA875 (Styphnate type) — Incomplete oxidation

$$0.1699 \ Ba(NO_3)_2(s) + 0.1466 \ CaSi_2(s) + 0.0877 \ C_6H(NO_2)_3O_2Pb(s)$$

$$+ 0.0833 \ C(s) \longrightarrow 0.1699 \ BaO(g) + 0.1466 \ CaO(l)$$

$$+ 0.0877 \ PbO(g) + 0.2932 \ SiO_2 \ (l,g) + 0.5325 \ CO(g)$$

$$+ 0.0770 \ CO_2(g) + 0.0439 \ H_2O(g) + 0.3015 \ N_2(g) \tag{8}$$

FA875 (Styphnate type) — Complete oxidation

$$0.1699 \ Ba(NO_3)_2(s) + 0.1466 \ CaSi_2(s) + 0.0877 \ C_6H(NO_2)_3O_2 \ Pb(s)$$

$$+ 0.0833 \ C(s) + 0.2663 \ O_2(g) + 1.2169 \ N_2(g) \longrightarrow$$

$$0.1699 \ BaO(g) + 0.1466 \ CaO(l) + 0.0877 \ PbO(g)$$

$$+ 0.2932 \ SiO_2(g) + 0.6095 \ CO_2(g) + 0.0439 \ H_2O(g)$$

$$+ 1.5184 \ N_2(g) \tag{9}$$

FA70 (Chlorate type)*   –   Incomplete oxidation

$$0.4323 \ KClO_3(s) + 0.0500 \ Sb_2S_3(s) + 0.0773 \ Pb(CNS)_2(s)$$

$$+ \ 0.0220 \ C_6H_2(NO_2)_3(CH_3)(s) \longrightarrow 0.4323 \ KCl(g)$$

$$+ \ 0.0500 \ Sb_2O_3(g) + 0.0773 \ PbO(g) + 0.3046 \ SO_2(g)$$

$$+ \ 0.0798 \ CO(g) + 0.2288 \ CO_2(g) + 0.0550 \ H_2O(g)$$

$$+ \ 0.1103 \ N_2(g) \tag{10}$$

FA70 (Chlorate type)*   –   Complete oxidation

$$0.4323 \ KClO_3(s) + 0.0500 \ Sb_2S_3(s) + 0.0773 \ Pb(CNS)_2(s)$$

$$+ \ 0.0220 \ C_6H_2(NO_2)_3(CH_3)(s) + 0.0399 \ O_2(g)$$

$$+ \ 0.1823 \ N_2(g) \longrightarrow 0.4323 \ KCl(g) + 0.0500 \ Sb_2O_3(g)$$

$$+ \ 0.0773 \ PbO(g) + 0.3046 \ SO_2(g) + 0.3086 \ CO_2(g)$$

$$+ \ 0.0550 \ H_2O(g) + 0.2926 \ N_2(g) \tag{11}$$

FA90 (Chlorate type)*   –   Complete oxidation

$$0.4323 \ KClO_3(s) + 0.0353 \ Sb_2S_3(s) + 0.0773 \ Pb(CNS)_2(s)$$

$$+ \ 0.0316 \ C(CH_2NO_3)_4(s) \longrightarrow 0.4323 \ KCl(g)$$

$$+ \ 0.0353 \ Sb_2O_5(g) + 0.0773 \ PbO(g) + 0.2605 \ SO_2(g)$$

$$+ \ 0.3126 \ CO_2(g) + 0.1264 \ H_2O(g) + 0.0749 \ O_2(g) + 0.1405 \ N_2(g) \tag{12}$$

---

*The assumption that the oxide, rather than the sulfide, of lead exists at the flame temperature is not in conflict with the previously reported finding of lead sulfide in the product residue of the chlorate mixture. The nature of the explosive reaction probably was such that the maximum flame temperature was not attained; thus the assumed reaction does not completely describe the experimental results obtained.

The oxygen balance in the FA 90 primer mixture is sufficient to raise the products to their highest oxidation state compatible with the stability of the products. Excess oxygen is assumed to exist as $O_2(g)$. Under the above conditions, the calculated adiabatic flame temperatures are as follows.

Table X. Calculated Adiabatic Flame Temperatures

Primer Mixture	Condition	Adiabatic Flame Temperature (°K)
FA878	Incomplete oxidation	4080
	Complete oxidation	3940
FA875	Incomplete oxidation	2500
	Complete oxidation	2600
FA70	Incomplete oxidation	2520
	Complete oxidation	2600
FA90	Complete oxidation	2660

The Franklin Institute[2] has determined, by sodium line reversal techniques, the maximum temperatures attained when FA90, P4, and styphnate type primer mixtures were fired under unconfined conditions. The styphnate type primer (40 per cent lead styphnate, 40 per cent barium nitrate, 7.5 per cent calcium silicide or antimony sulfide, 7.5 per cent lead dioxide, and 5 per cent tetrazine) exhibited a temperature of 2405° K at a point approximately one inch in front of the primer cavity. The P4 type primer mixture (17.5 per cent red phosphorus, 77 per cent barium nitrate, 5 per cent trinitrotoluene, and 0.5 per cent aluminum hydroxide) exhibited a temperature of 2385° K under the same conditions. The FA90 primer mixture, on the other hand, showed a peak temperature of only 1900° K, but the accuracy of this value was in doubt. Firing of these primers under constant volume conditions would undoubtedly cause them to exhibit a higher temperature, but it is difficult to estimate the magnitude of the increase.

In regard to Table X, it is seen that the FA878 mixture exhibits, by far, the highest calculated flame temperature. While the effect of molecular dissociation of the product gases is significant at 4000° K, it will not serve to reduce the calculated temperature by more than a few hundred degrees. Thus, the zirconium type primer mixture (FA878) which possesses, generally speaking, the best over-all ignition properties of the three types (zirconium, chlorate, and styphnate) also exhibits the highest flame temperature.

The energies evolved by the postulated reactions, as calculated from the heats of formation of the reactants and products at room temperature, are presented in the following table:

Table XI. Heats of Reaction at 298° K of Primer Mixtures

Primer Mixture	Condition	Calculated $\Delta H_R^{298°K}$ (kcal/100 grams)
FA878	Incomplete oxidation	106.6
	Complete oxidation	140.7
FA875	Incomplete oxidation	67.8
	Complete oxidation	103.6
FA70	Incomplete oxidation	65.2
	Complete oxidation	70.5
FA90	Complete oxidation	68.8

Wilkinson[3] determined the heat of reaction of the FA70 mixture to be 60.5 kcal/100 grams, a value closer to the calculated heat of reaction for the condition of incomplete oxidation than to that for the condition of complete oxidation. The same author[3] determined the heat of reaction of a styphnate primer mixture to be 78.8 kcal/100 grams. While the composition of this mixture (38 per cent barium nitrate, 40 per cent lead styphnate, 10 per cent calcium silicide, 9 per cent lead dioxide, and 3 per cent graphite) is slightly different from that of the FA875 primer mixture, it is seen that the experimental heat of reaction is closer to the calculated value for the condition of incomplete oxidation. It therefore appears that the styphnate and FA70 chlorate primer explosions are characterized by incomplete oxidation; namely, that only the oxygen initially present in the primer mixture enters into the reaction.

It is seen that the zirconium type primer mixture (FA878) exhibits a higher calculated heat of reaction than do any of the other types, indicating the heat of reaction may also be a factor of importance in determining the ignition properties of a primer.

While all the inorganic products of the chlorate type mixtures undoubtedly are vaporized at the flame temperature, this is not the case with the styphnate and zirconium type primer mixtures. In the latter, zirconium dioxide, the largest constituent of the primer products, exists in the molten state at the calculated flame temperature; while in the former calcium oxide alone exists in the molten state for the condition of complete oxidation. Assuming incomplete oxidation, both calcium oxide and a small amount of silicon dioxide are molten. The molten products of the styphnate primer explosion,

while comprising a significant part of the products, do not constitute as much on a comparative basis as does zirconium dioxide in the zirconium type mixture. Bearing in mind the fact that liquids exhibit greater heat transfer properties than do gases, it is seen that the zirconium type mixture has the largest amount of its products in the liquid state at the flame temperature.

Undoubtedly, there is no one particular characteristic which is all important in determining the ignition properties of a primer mixture. However, the fact that the zirconium type mixture, FA878, which has the best ignition properties of the three types discussed, exhibits the following characteristics:

(1) Highest calculated adiabatic flame temperature,

(2) Highest heat of reaction, and

(3) Largest amount of molten particles in the primer products at the flame temperature,

points to the significance of these factors in determining the propellant ignition properties of primers.

Subsequent to the completion of the calculations in this report, a report by Lenchitz[20] was received in which the heats of reaction, flame temperatures, and products of reaction of the M1A1 and modified M1A1 squibs were determined. It was concluded by the author that the greater efficiency of ignition, as exhibited by the latter, was due to a higher heat of reaction per mole of gas produced, a higher flame temperature, and a greater quantity of solid particles formed by the reaction of the modified M1A1 squib. As shown above, these factors are also of importance in determining the propellant ignition properties of primers in small arms.

CONCLUSIONS

1. The calculated adiabatic flame temperatures of the several primer mixtures are as follows.

Primer Mixture	Type	Condition	Adiabatic Flame Temperature, (°K)
FA878	Zirconium	Incomplete oxidation	4080
		Complete oxidation	3940
FA875	Styphnate	Incomplete oxidation	2500
		Complete oxidation	2600
FA70	Chlorate	Incomplete oxidation	2520
		Complete oxidation	2600
FA90	Chlorate	Complete oxidation	2660

2. The zirconium type mixture exhibits the highest flame temperature, as shown above, the highest heat of reaction at 298° K, and possesses the largest amount of primer products in the molten state at the calculated flame temperature. In view of the fact that the zirconium primer mixture exhibits the best ignition properties, it is suggested that the above three factors are of importance in determining the pro- pellent ignition characteristics of a primer.

RECOMMENDATIONS

It is recommended that

1. The heat of reaction of the zirconium type primer mixture be determined.

2. Basic data necessary to permit accurate calculations of various thermochemical properties of primer mixtures be determined.

3. Mixtures whose explosions are characterized by high flame temperatures, high heats of reaction, and whose products exist in the molten state at these flame tempera- tures (i. e., very high melting and boiling points) be investigated for use as primers.

31

BIBLIOGRAPHY

(1) Rechel, E. R., "Small Arms Primers," Frankford Arsenal Laboratory Report No. 10, March 1932.

(2) "Investigation of Primers," Franklin Institute Final Report, 9 March 1950 to 9 May 1950.

(3) Wilkinson, R. F., "The Thermochemistry of Priming Mixtures," Frankford Arsenal Report R-970, April 1950.

(4) Kirshner, H. A., "Chemical Balance of the P4 Primer," Frankford Arsenal Report R-987, October 1950.

(5) Hirschfelder, J. O.; McClure, F. T.; Curtiss, C. F.; Osborne, D. W.; "Thermodynamic Properties of Propellent Gases," National Defense Research Committee Report No. A-116, November 1942.

(6) "An Instrument for Determination of Transient Flame Temperatures," Institute of Industrial Research, University of Denver, Phase Report No. 4, 3 June 1952.

(7) Wilkinson, R. F., "Basic Research on Incendiary Ignition, Part IV - Flame Temperature of Incendiary Mixtures," Frankford Arsenal Memorandum for Record, August 1949.

(8) Singley, J. E., Jr.; and Fohrell, E. H., Jr.: "Theoretical Study of Lithium and Boron Compounds as High Energy Reducing Agents in Solid Propellants," Redstone Arsenal Report T-4-a, 31 October 1951.

(9) "Report on Study of Pure Explosive Compounds. Part IV - Calculation of Heat of Combustion of Organic Compounds from Structural Features and Calculation of Power of High Explosives," Arthur D. Little, Inc., May 1952.

(10) Fischer, M. J., and Snay, H. G., "Heat Capacities for Calculations of Explosion Phenomena," Naval Ordnance Laboratory, Navord Report 1804, 1 May 1952.

(11) "Investigation of Primers," Franklin Institute Progress Report, 16 August 1951 to 24 October 1951.

(12) "X-ray Diffraction Patterns," American Society for Testing Materials.

(13) Rossini, F. D.; Wagman, D. D.; Evans, W. H.; Levine, S.; and Jaffe, I.; "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular No. 500, February 1952.

BIBLIOGRAPHY (Cont'd)

(14) Kelley, K. K., "Contributions to the Data on Theoretical Metallurgy. II. High Temperature Specific Heat Equations for Inorganic Substances," Bureau of Mines, Bulletin 371, 1934.

(15) Thompson, M. K., "The Total and Free Energies of Formation of the Oxides of Thirty-two Metals," The Electrochemical Society, Inc., 1942.

(16) Harvalik, Zaboj V., "Explosive Initiators, Electric. A Literature Survey," Bureau of Ordnance, Navord Report 1487, June 1950.

(17) *Handbook of Chemistry and Physics*, 32d Edition, Cleveland, Ohio, Chemical Rubber Publishing Co., 1951.

(18) Urey, H. C., *The Planets*, New Haven, Conn., Yale University Press, 1952.

(19) Bichowsky, F. R., and Rossini, F. D., *The Thermochemistry of Chemical Substances*, New York, N. Y., Reinhold Publishing Corp., 1936.

(20) Lenchitz, C., "A Study of the Influence of Several Chemical and Thermodynamic Properties on the Ignition Efficiency of the M1A1 Squib and the M1A1 Squib Loaded with Modified T61 Composition," Picatinny Arsenal Report 1940, 19 June 1953.

Distribution

1 - Chief of Ordnance
Department Army
Washington 25, D. C.
Attn: ORDTX-AR

1 - Attn: ORDTS

1 - Attn: ORDIS

1 - Attn: ORDTA - Propellant and
Primer Section

1 - Attn: ORDTU

1 - Commanding Officer
Springfield Armory
Springfield 1, Mass.
Attn: Eng Dept

1 - Commanding General
Picatinny Arsenal
Dover, New Jersey
Attn: Tech Group

1 - Attn: Library

1 - Commanding Officer
Rock Island Arsenal
Rock Island, Ill.
Attn: Laboratory

1 - Commanding Officer
Watertown Arsenal
Watertown 72, Mass.
Attn: Tech Group

2 - Commanding General
Redstone Arsenal
Huntsville, Alabama
Attn: Technical Library

3 - Commanding General
White Sands Proving Ground
Las Cruces, New Mexico
Attn: Technical Librarian

2 - Commanding General
Aberdeen Proving Ground
Maryland
Attn: Ball Res Lab
ORDBG-BLI

1 - Commandant
Ordnance School
Aberdeen Proving Ground
Maryland
Attn: Tech Intell Br

1 - Attn: ORDHS-RC

1 - Commanding Officer
Office of Ordnance Research
Box CM, Duke Station
Durham, N. C.

5 - Armed Services Technical
Information Agency
Document Service Center
Knott Building
Dayton 2, Ohio
Attn: DSC-SD
(Code 1)

1 - Department of the Air Force
Hq USAF, DCS/D
Washington 25, D. C.
Attn: AFDRD-AR

1 - Attn: AFDRD-AN
Maj H. R. Schmidt

1 - Commanding General
Wright Air Development Center
Wright-Patterson Air Force Base
Dayton, Ohio
Attn: WCFGH-2

1 - Attn: WCLPN-2

1 - Attn: WCRRC

Distribution (Cont'd)

1 - Department of the Navy
Bureau of Ordnance
Washington 25, D. C.
Attn: Ad3, Tech Library

1 - Attn: Re2a

tn: Re2d

1 - Commander
U. S. Naval Air Missile
Test Center
Point Mugu, California
Attn: Tech Library

2 - Commanding Officer
U. S. Naval Powder Factory
Indian Head, Maryland
Attn: Res and Devel Dept

1 - Commander
U. S. Naval Proving Ground
Dahlgren, Virginia
Attn: M. I. Division

1 - Commander
U. S. Naval Ordnance Laboratory
White Oak
Silver Spring, Maryland
Attn: Library

3 - Commander
U. S. Naval Ordnance
Test Station
Inyokern, China Lake
California
Attn: Tech Library Br

1 - Commanding Officer
Office of Naval Research
Branch Office
86 E. Randolph Street
Chicago 1, Illinois
Attn: LTJG M. C. Laug

1 - Commanding Officer
Office of Naval Research
1030 E. Green Street
Pasadena 1, California

1 - Bureau of Mines
4800 Forbes Street
Pittsburgh 13, Pa
Attn: Explosives and
Physical Sciences Div

1 - Aerojet-General Corporation
P. O. Box 296
Azusa, California
Attn: Librarian

1 - Allegany Ballistics Laboratory
P. O. Box 210
Cumberland, Maryland

1 - Armour Research Foundation of
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois
Attn: Propulsion and Structures
Research
Department M

1 - Catholic University of America
7th St. and Michigan Ave., N. E.
Washington 17, D. C.
Attn: F. O. Rice

1 - E. I. du Pont de Nemours
and Company
10th and Market Streets
Wilmington, Delaware
Attn: W. F. Jackson

1 - The Franklin Institute
20th and Parkway
Philadelphia 3, Pennsylvania
Attn: Chem Kinetics and
Spectroscopy Section
W. E. Scott

36

Distribution (Cont'd)

1 - Hercules Experiment Station
    Wilmington, Delaware
    Attn: A. M Ball

1 - Director
    Jet Propulsion Laboratory
    4800 Oak Grove Drive
    Pasadena 3, California

1 - Arthur D. Little, Inc.
    30 Memorial Drive
    Cambridge 42, Mass
    Attn: W. A. Sawyer

1 - Attn: W. C. Lothrop

1 - Midwest Research Institute
    4049 Pennsylvania
    Kansas City, Missouri
    Attn: Tech Director

1 - University of Michigan
    Engineering Research Institute
    Ann Arbor, Michigan
    Attn: J. C. Brier

1 - Naval Ordnance Research
    School of Chemistry
    University of Minnesota
    Minneapolis 14, Minnesota
    Attn: B. L. Crawford, Jr.

1 - Project Squid
    Princeton University
    Princeton, New Jersey
    Attn: Librarian

1 - Purdue University
    Department of Chemistry
    Lafayette, Indiana
    Attn: H. Feuer

1 - Rohm and Haas Company
    5000 Richmond Street
    Philadelphia 37, Pennsylvania
    Attn: J. F. Kincaid

1 - Rohm and Haas Company
    Redstone Arsenal Research Div
    Huntsville, Alabama
    Attn: Tech Director

3 - Solid Propellant Information Agency
    Applied Physics Laboratory
    The Johns Hopkins University
    Silver Spring, Maryland
    Attn: P. K. Reily, Jr.

1 - Standard Oil Company
    Research Department
    P. O. Box 431
    Whiting, Indiana
    Attn: W. H. Bahlke

2 - Thiokol Chemical Corporation
    Redstone Arsenal
    Huntsville, Alabama
    Attn: Tech Director

1 - Thiokol Chemical Corporation
    Elkton Division
    Elkton, Maryland
    Attn: D. W. Kershner

1 - Western Cartridge Company
    East Alton, Illinois
    Attn: R. L. Womer

1 - Shell Development Company
    Emeryville, California
    Attn: S. S. Sorem

1 - Southwest Research Institute
    Department of Chemistry and
    Chemical Engineering
    8500 Culebra Road
    San Antonio 6, Texas
    Attn: J. H. Wiegand

1 - Remington Arms Co., Inc.
    Bridgeport, Conn.

37

Armed Services Technical Information Agency

Because of our limited supply, you are requested to return this copy WHEN IT HAS SERVED YOUR PURPOSE so that it may be made available to other requesters. Your cooperation will be appreciated.

AD

41152

Reproduced by

DOCUMENT SERVICE CENTER
KNOTT BUILDING, DAYTON, 2, OHIO